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Novel Swelling Structures and Electromotility Response in Polyelectrolyte Gels

Dana Deardorff
Illinois Wesleyan University

Novel Swelling Structures and Electromotility Response in Polyelectrolyte Gels

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by

Dana Deardorff

to
Department of Physics

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Bloomington, IL 61702-2900

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Advisor: Dr. Narendra K. Jaggi

SYNOPSIS

The research described herein might be somewhat unique in the fact that it is not an isolated "project." Rather, it comprises over two years of interdisciplinary studies conducted in the Laboratory for Materials Physics at Illinois Wesleyan University. I have intentionally not included results from other research experiences at Michigan State University and at Hampshire College. I have compiled four papers which detail some of the exciting developments that have occurred in our work. All four papers are related to the structures, dynamics, electric response, and pattern formation in polyelectrolyte gels. I have been fortunate enough to experience work which led to legitimate discoveries and publishable material. The first two papers are already in print in "The Journal of Undergraduate Research in Physics," a refereed publication of the American Journal of Physics. The other two papers are in the process of being submitted to another research journal. It therefore seemed appropriate for these papers to simply be included in their entirety, without further commentary. They are a legitimate compilation of the most notable findings.

The first paper, "Polyelectrolyte Gels as Artificial Muscle Systems," focuses on the large electromotility response exhibited by these gels. Although it does not include a discussion of many of our initial struggles in working with these gels, it highlights our understanding of the underlying physics of the phenomenon of bending in response to electric fields. Our findings show that the fundamental mechanism for bending is diffusional in nature. However, we also found that the actual bending is not always regular and sometimes exhibits unusual motions during repetitive bending.

During these electromotility studies, we discovered, almost accidentally, that these gels swell inhomogeneously. The second paper, "Art in Physics: Exotic Macrostructures in Swelling Polyelectrolyte Gels," provides a qualitative understanding of the

physical process that produces elegant structural changes during swelling. Although the surface patterns and shape transformations are complex, they are essentially reproducible. In order to quantify the swelling transitions, we focus on the fringe pattern that develops at the edge of the gel during swelling and measure the temporal evolution of the dominant wave vector characterizing the structures. Further, these gels can also be appreciated purely for their aesthetic appeal. As they continue to swell, they create an ever-evolving artistic forum. We are planning an "art" exhibit of photographs of these elegant and aesthetic forms.

The third and fourth papers are draft versions describing very recent work. We recognize that they need substantial editorial revision. It was, however, considered important to include them, for the sake of completion, in this honors thesis. Both papers are extensions of the work described in the second paper - attempts to better understand and quantify the nature of the structural changes during swelling. "Structural Formations in Swelling Gels: The Fold Pattern Formation on the Edges of Unrestrained Gel Cylinders" is a closer look at the evolution of the fringe pattern. This paper focuses on that fringe pattern and the fundamental differences between previous work on 2-dimensional surfaces and the 3-dimensional structures. "Dependence of Surface Patterns on the Elastic Moduli of Polyelectrolyte Gels" focuses on the effects of the initial gel composition upon the resulting swelling patterns. It also provides analysis of the variation in pattern formation during the early time swelling. New morphologies of the evolving surface patterns have been discovered. Another interesting finding of this research was the discovery of an apparent "memory effect" in the development of the pattern formation.

The Journal of Undergraduate Research in Physics

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POLYELECTROLYTE GELS AS ARTIFICIAL MUSCLE SYSTEMS

Kimberly Branshaw, Dana Deardorff and Garrett Davis
Laboratory for Materials Physics
Illinois Wesleyan University
Bloomington, IL 61702-2900
received June 28, 1994

ABSTRACT

Electromotility, the bending in response to an electric field, of polyelectrolyte gels in ionic solutions has been identified as a candidate for a potential chemomechanical engines such as muscles. We discovered that the underlying physics of these systems is more complex than previously believed. We found that the bending as a function of time obeys a square root power law. This points strongly towards a diffusion mechanism for the bending. Kinetic evidence for diffusion was independently corroborated by experiments on gels grown or bent in the presence of dyes. We explored the effects of varying poly-ion concentration in the backbone of the polymer and in the surrounding medium. In some cases, the electromotility cannot be described as simple bending.

INTRODUCTION

Traditionally, it requires two steps to convert chemical energy into mechanical energy. First, a battery or power plant converts chemical energy into electric energy, which in turn drives a motor to produce kinetic energy. There is significant interest in integrating these two steps into one and making a "chemomechanical engine". A naturally occurring chemomechanical engine is muscle tissue. During the past nine years, polyelectrolyte gels in ionic solutions have been investigated as artificial muscle-like materials. [1,2,3] These gels undergo large reversible bending motions in response to an applied electric field.

Kimberly is a senior with a double major in physics and chemistry. She has won the best undergraduate research presentation award at two consecutive annual meetings ('94 and '95) of zone 9 of the Society of Physics students. She will attend graduate school in materials science, probably at Northwestern University.
Dana is a senior physics major. This research, which was presented at two national conferences, resulted in a strong interest in biomechanics and other areas of physics in biomedicine. He is planning to attend graduate school in biomedical engineering at UC-Berkeley.
Garrett received his bachelor's degree from IWU in 1994 and is enrolled in the 3-2 dual degree program. He will receive a B.S. in electrical engineering this summer from Washington University and will probably go on to graduate school.

A gel is a state of matter that is intermediate between a liquid and a solid. Gels have properties of both of these states of matter. They support a shear stress like solids, but still allow mass and charge diffusion like liquids. A polymer is a chain of basic chemical units, called monomers, that are covalently linked together in a solvent. In the solvent, the polymer chains behave like a highly viscous liquid. If the polymerization process occurs in the presence of a cross linking agent, two monomer units joined by a side chain, permanent links would be formed at random positions between the long polymer chains in the solvent. This creates a complex network of branches and interconnections.[4] At this point, if the solvent were allowed to evaporate from the polymer, a hard solid would result.

If these polymers are allowed to become swollen with a solvent, they become gels. The solvent is held inside the gel by a hydrophilic network of these long cross linked chains. [4] The gels have solid-like properties due to the geometrical constraints enforced by the cross linked network of polymer, yet display liquid-like properties due to the free flowing solvent within the solid-like structure. The structure of the gel is maintained by the electrostatic repulsions of the side linking chains and the osmotic pressure caused by the ions in the solvent. [4]

THE EXPERIMENT

Preparation of the gels

The gels were prepared in the following way. Acrylic acid, acrylamide, sodium hydroxide and

N,N-methylenebisacrylamide were dissolved in water with mole ratios of 0.1, 0.1, 0.1 and 0.001 respectively to make a total volume of 50 ml. 50 mg of potassium persulfate and 0.2 ml of N,N,N'N'-tetramethylethlyenediamine (TEMD) were added to this mixture to polymerize the gels.[5] The gelation time was dependent on the concentration of the potassium persulfate and TEMD, the temperature of the solution and the volume of the gel made. In our case, the gelation time ranged between 5 and 15 minutes and the solution temperature was approximately 60 C.

For electromotility measurements, these gels were cast in 1.5 mm glass capillary tubes and removed either by pumping water through them with a syringe or shattering the capillary tube. The polymerized specimens are then swollen in deionized water for a few hours to acquire their equilibrium volume. After swelling, the rods are approximately 6 mm in diameter. They can be cut with a sharp razor blade to produce specimens of desired lengths. They tend to be a bit brittle and the cut edges are not smooth.

Electromotility Measurements

The gels are put into a conductive aqueous solvent, usually water and then placed between two parallel carbon electrodes. A DC voltage between 5 V and 50 V was applied across the electrodes which induced a current less than 150 mA through the gel. The gels have a refractive index very close to that of water. They are barely visible when submerged. Video macroscopy and computerized image processing were used to delineate the contours of the rod shaped specimens. We measured the bending (deflection) produced by the electric field as a function of time. Figure 1 shows the two enhanced video images of the apparatus. The top electrode is the anode.

The measurements were done with gels of the same diameter, but a range of lengths. We also tried different concentrations of the conductive aqueous solvent, from deionized water to 0.1 M NaCl and changed the initial shape by cutting the original gel.

RESULTS

When the voltage was applied to the apparatus, the gel began to bend towards the anode. When the polarity was switched, the gel came back to a straight shape and began to bend towards the bottom electrode. Figure 2 shows a gel that has been subjected to an electric field for approximately 5 minutes. The polarity of the field was then switched. Each successive frame had this new polarity. The time interval between each frame is 90 seconds. The total time it takes for a gel to flex from one direction to the other was between 10 to 15 minutes. This confirms that the bending depends upon the direction of the applied electric field.[1,2,3] These pictures demonstrate both the promise and the problem of using these gels as artificial muscles. To be usable in engineering applications, the bending time must be decreased to a few fractions of a second.

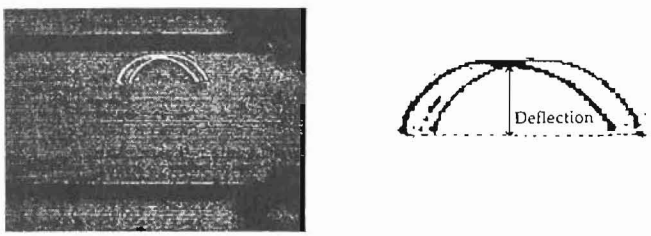

Figure 1
Two video images showing the electric field induced bending of the gels. The anode is the upper electrode. The two frames show different stages of video enhancement.

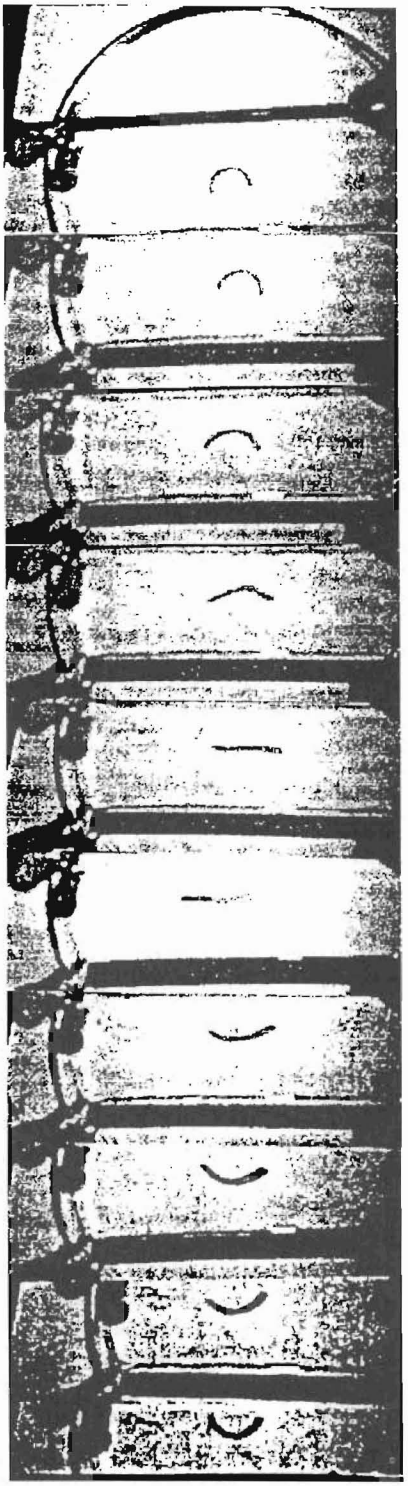

Figure 2
Flexing of a gel by reversing the direction of the electric field. there is about 90 sec time interval between each successive frame. The total time required for one bending sequence is approximately 15 min.

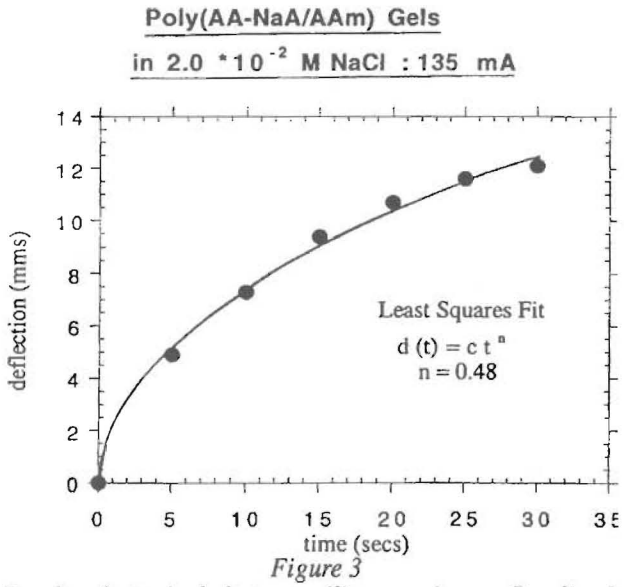

Figure 3

Results of a typical electromotility experiment. Bending is plotted as a function of time. The curve shown is a least squares fit to a simple power law function.

When the electric field is reversed, some gels show a rather complex bending behavior. On occasion, as the curvature of the gel is decreasing, the gel rod would roll about an axis parallel to its long edge. The bending always stayed consistent with the direction of the applied electric field, but the gel avoided the intermediate stages of straightening out. Other gels, go through an intermediate "S" shape before beginning to curve in the opposite direction. We will continue to examine this interesting behavior.

Figure 3 is a typical plot of the bending, d, as a function of time, t. The line drawn was a least squares fit to the data with a simple power law:

$$d(t) = c\, t^n \,. \qquad (1)$$

The different samples produced an exponent n between 0.48 and 0.55. These exponents were close enough to 0.50 for us to suggest that the bending was dependent upon the square root of the time. This dependence is strongly suggestive of a diffusional mechanism for the bending. It has been suggested that the bending results from diffusion of water into one side of the gel. That side of the gel then begins to expand more than the other side and bends to accommodate the differential swelling. The direction of the electric field determines into which side of the gel the water diffuses. The result is similar to that of a heated bimetal strip.

To directly demonstrate the diffusion process, dyes were introduced into the gel in two different ways. The dye was either dissolved in the water used to swell the polymerized and cross linked material or it was introduced into the monomer solutions used as precursors. When the swelled dyed gels were placed in undyed water, passive diffusion of the dye out of the gel occurred over a period of a few days. This showed that any passive diffusion of the dye during the few minutes that it takes for the electromotility measurements was not important.

The charge neutrality of the dyes was tested by placing them in the solvent and applying an electric field. No electrophoresis was noticed. This indicated that the dyes are charge neutral, but does not rule out the possibility that the dye molecules interact with the charge back bone of the polymer and acquire a charge when incorporated in the

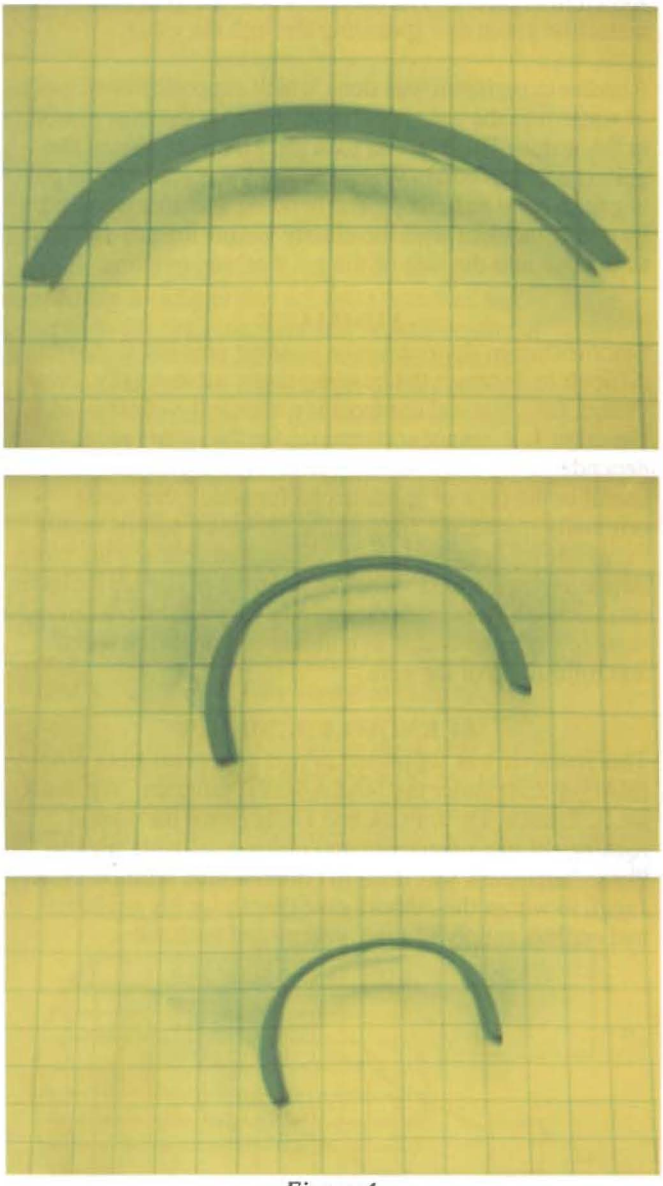

Figure 4

Direct observation of a diffusinal mechanism for the bending action. The gel was grown in the presence of malachite green dye. The dark areas near the gels are the dye diffusing out of the gel and into the clear surrounding water.

gel. We used two dyes: safranine O and malachite green. The bending kinetics of the dyed gels were found to have the same square root dependence on time as the undyed gels.

While the electromotility experiment is in progress, the dye begins to diffuse out of the gel and into the surrounding water in a matter of minutes as the bending occurs. The gel then began to appear as one part containing the dye and the other part that was clear. The diffusion of the dye into the surrounding solvent provided direct evidence of the diffusional process. Examples of this diffusion are shown in Figure 4. The dark area near the gels is the malachite green dye spreading through the water.

Another experiment was done which supports the diffusion of water into the gel. A gel containing no dye was placed in the water. The dye was then placed on the side of the gel expected to bend. When the field was applied, the gel began to bend as before. The bending was accompanied by and coincident with the clearly visible inward diffusion of the dye into the side of the gel that was swelling.

SUMMARY

Since diffusion dominates the bending process, it may be difficult to decrease the bending times substantially. Even though the chemical composition affects the constant in Equation 1, it cannot compensate for the square root dependence on time. Consequently, these gels may not be useful in the type of applications for which they were originally intended. They might, however, still be usable in 'gentle robotics', where precision and delicacy are more important than speed. Work in progress in our lab includes modification of the side chains and varying the concentrations of the cross-linker as a means of improving speed and robustness of the gels.

ACKNOWLEDGMENTS

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Dr. N.K. Jaggi
Laboratory for Materials Physics
Illinois Wesleyan University
Bloomington, IL 61702-2900

ART IN PHYSICS: EXOTIC MACROSTRUCTURES IN SWELLING POLYELECTROLYTE GELS

Dana Deardorff and Kimberly Branshaw
Department of Physics
Laboratory for Materials Research
Illinois Wesleyan University
Bloomington, IL 71702

received July 10, 1994

ABSTRACT

We have recently discovered, somewhat accidentally, a rare and elegant coarsening mode in the swelling of some polyelectrolyte gels that leads to intermediate structures that are quite complex and beautiful. These gels evolve from simple cylindrical shapes in the beginning to form periodic patterns of "cusps" around the edges and roughening of the surface at short times. At intermediate stages, the elegant, three-dimensional structures formed resemble a sensuous orchid. Finally, the gel returns to its original geometry as a scaled-up replica of the initial structure. Curiously, the intermediate structures, however complex, are quite reproducible in all essential features. The results and our qualitative understanding of this phenomenon are presented.

INTRODUCTION

There has been considerable interest in the past few years in the electromotility (the phenomenon of bending in response to an electric field) of polyelectrolyte gels, [1,2] Polyelectrolyte gels are a class of cross linked polymers[1] that swell considerably when placed in a solvent, up to 60 times their initial volume.

To understand the swelling process, consider the gel cylinder to be divided into a grid of smaller sections, shown in Figure 1. Each section represents a part of the gel to be swelled with water. The concentration of water into the gel has a diffusional profile and decreases as one moves inward from the periphery of the gel. Thus, a section near the center will not swell much, while a section near the periphery will swell considerably. Because all the sections near the periphery want to swell substantially, there is not sufficient space for them to grow uniformly. The geometrical space constraint of the gel itself forces the edges to "buckle" as they continue to swell.

Research is in progress to utilize these gels as artificial muscles. [2,3] Because of their intended use as artificial muscles, prior research was conducted using tiny rod-shaped gels. Through experimentation with a much larger cylindrical piece, we discovered an unusual and interesting

Dana is a senior physics major with a strong parallel interest in art. This work was stimulated by this eclectic interests in art and physics and has been presented at two national conferences. He is planning to attend graduate school in Biomedical engineering at UC-Berkeley.

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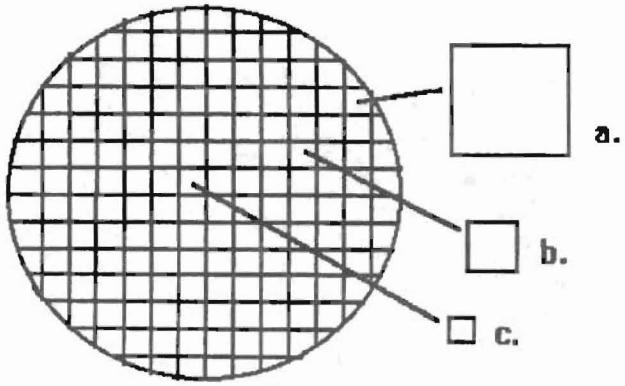

Figure 1
Schematic drawing of gel cylinder illustrating the swelling of different sections.

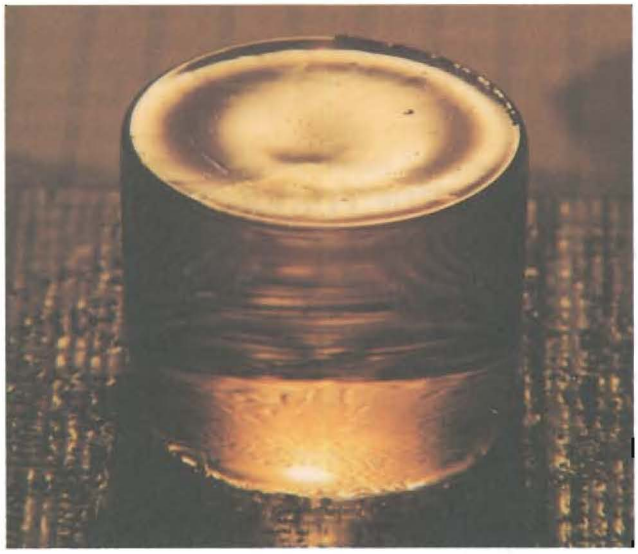

Figure 2
Photograph of the unswollen cylindrical gel. The diameter is 38 mm.

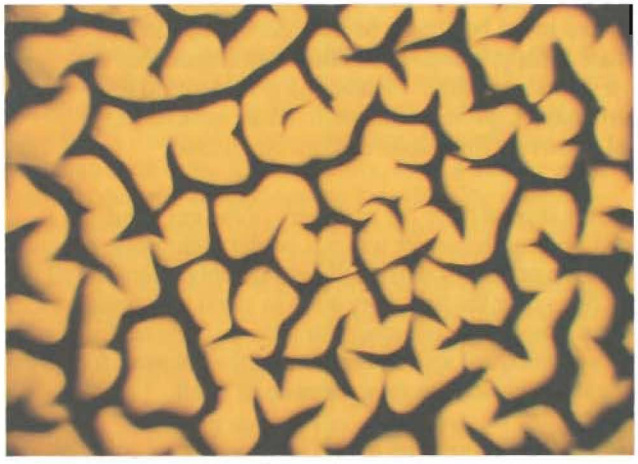

Figure 3b
Initial coarsening of the surface of the gel

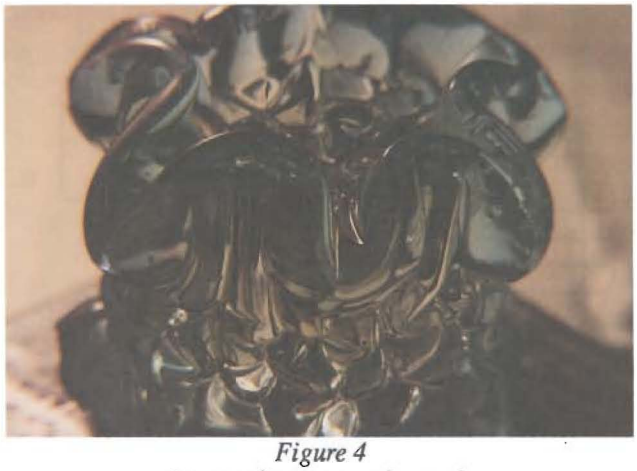

Figure 4
Intermediate state of growth.

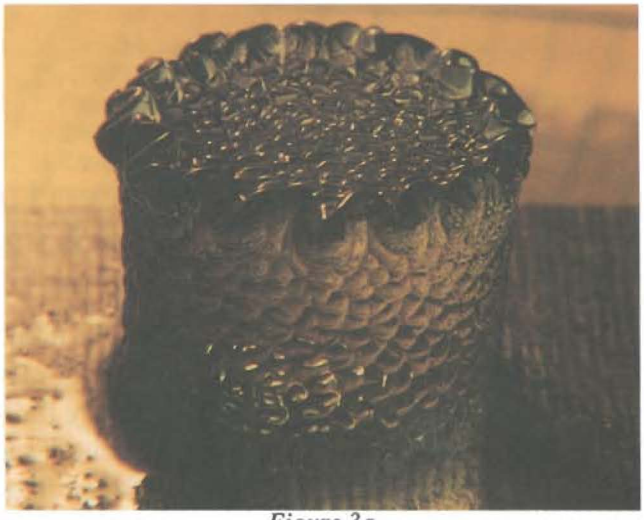

Figure 3a
Early stages of the swelling of the gel

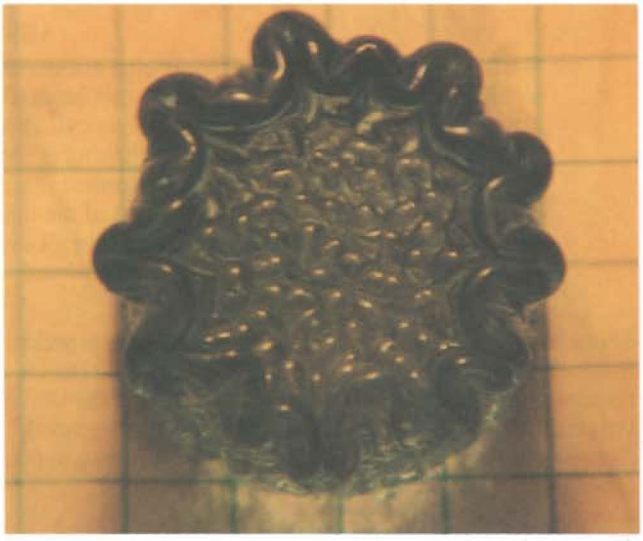

Figure 3c
"Fold pattern" at the top edge of the cylindrical gel.

Figure 5
Final stage of the growth, showing the return to original shape. The diameter is now approximately 120 mm.

Figure 6a

Photographs of the intermediate state of a swelling gel containing a dye. The 'sculpture' in Figure 6 was illuminated with white light while the 'sculpture' in Figure 7 was illuminated with from the back with a red night lamp and a regular frosted light bulb.

Figure 6b

phenomenon. Even though the final swollen gel has the same geometry as the starting shape of the gel, we discovered, almost accidentally, that the swelling is quite inhomogeneous during the intermediate stages. These gels undergo structural swelling transitions that are rare and quite elegant. The resulting structural forms of the gels are interestingly complex.

THE EXPERIMENT

Experiments were conducted using the cross linked Poly (AA-NaA/AAm) polyelectrolyte copolymer gel, where AA is acrylic acid, NaA is sodium acrylate, and AAm is acrylamide, with water as the swelling medium. Although other gel geometries were investigated, our research was focused primarily on right cylindrical gel pieces of varying diameter. When swollen, the gel's refractive index is nearly identical to that of water, making the gel almost invisible when submerged. Frequently so two neutral dyes, safranine-O and malachite green, were added to improve the visibility of the swollen gels. Observations and measurements were taken using still photography and video macroscopy. Complete details of the chemical composition and procedures to synthesize these gels can be found in another paper in this volume that focuses on the responses of these materials to electric fields. [3]

STRUCTURAL EVOLUTION

We have divided the swelling process into three main characteristic stages of growth. The time scale for these structural changes in not fixed, but depends upon the initial size, shape and chemical composition of the gel. The time scales indicated in parentheses in the following descriptions correspond to a typical experiment starting with a right cylindrical piece of the PAA gel with a diameter of 38 mm as shown in Figure 2.

Early Stage (several minutes).
During this initial swelling, there is not much change in the total volume. However, there is an almost immediate appearance of roughening or coarsening on all the free surfaces of the gel as seen in Figure 3a and Figure 3b. There is emergence of periodic points or "cusps" around the edges of the gel, a structure which we call the "fold Pattern" because of its apparent tendency to fold into itself during further growth evolution, see Figure 3c. The entire fold pattern is itself quasiperiodic with each repeating part being wave like. Thus, we define a wave number, k, such that $k = 2\pi/\lambda$, where λ is the dominant length scale over which the pattern repeats. The early stage is distinguished by small λ or large k.

Intermediate Stage (several hours)
During this stage, there is considerable swelling and noticeable change in the volume. The swelling is dominated by the evolution of the fold pattern as the structural form of the gel is overtaken by substantial swelling of the folds themselves as shown in Figure 4. The structural changes are now occurring on a much larger length scale (λ). As the folds at the edges of the gel are growing and increasing in size, they are also systematically reducing in number as they "dissolve" into each other. Thus, the characteristic wave number $k(t)$ is decreasing monotonically with time.

Final Stage (several days)
During this stage, the get approaches its maximum swelling potential, approximately 60 times its original volume. As the fold pattern evolves, the structure becomes much less complex. Remarkably, each get "remembers" its shape and eventually returns to that original geometric form in this much larger, swollen state. After all of these unusual structural changes, the final product is an identical, scaled up version of the original gel's geometry as shown in Figure 5.

THE AESTHETICS

Apart from the obvious scientific importance of this discovery, one is captivated by the beauty of these delicate structures. It is not often that the worlds of art and science intersect so dramatically. These materials are chemically composed of simple polymer chains and are the product of a deterministic growth process. They are not the work of an artist, but still appear to be a "work of art". Figure 6 is an example of such a work of art. They possess a magnificent aesthetic quality. Their beauty is similar to ornate crystal or glass sculptures. At one stage, they resemble an exotic and translucent orchid. As they grow, they create an ever evolving artistic forum.

RESULTS AND DISCUSSION

Qualitative Results
At first sight, these complex patterns and transitions may seem almost chaotic or random. We have discovered, however, that the structural swelling transitions, despite their apparent complexity, are essentially reproducible. In particular, the shape transformations are basically identical for similar gel geometries. Two separate gels with similar initial shapes always evolve through the same stages of transitions.

Each gel identically follows the same "path" of structural changes each time it is swollen. At any stage during the swelling process, the gel can be removed from the water and allowed to return to its original, unswollen state. If the get is then replaced in water, it evolves following the same "path" of structural transitions as before.

Quantitative Results
Because the three-dimensional structural patterns and transitions are so intricate and complicated, we initially focus attention on one simple aspect. We look at the evolution of the fold pattern at the top edge of the gel cylinder as shown in Figure 3b. We measured the total number, N, of "cusps" or folds as a function of time for three different initial gel diameters: 22 mm; 32 mm; 38 mm. These data were then fit using a least squares analysis algorithm to a power law of the form:

$$N(t) = c\, t^{n} \quad . \qquad (1)$$

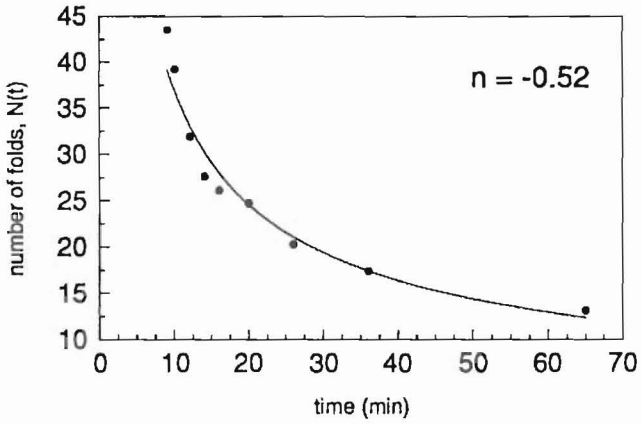

Figure 7
Evolution of fold-pattern of gel with diameter of 38 mm. The solid line is a fit to $N(t) = ct^n$.

The data and fit for one of these trials is shown in Figure 7. The three trials provided fits with exponents of n = -0.51, -0.53 and -0.52.

Since at any time, the wave number $k(t)$ is dependent upon the circumference of the cylinder of the gel itself, all trials were normalized to their initial diameter, d:

$$k = 2\,N/d \ . \qquad (2)$$

Thus, the size differences of the initial shapes were eliminated and all data could be compared and analyzed together as a "superset" . The results for all three trials are shown together in the logarithmic graph shown in Figure 8. The power law fit from these normalized data give an exponent of n = -0.50. We find that the fold pattern evolves in time as:

$$k(t) = c\ t^{-0.5} \qquad (3)$$

Previous experimental work on pattern formation in gels was done on two dimensional surfaces, thin, flat plates tethered on one side. [6] The experimentally observed exponent in these cases was also -0.5, the same as we found in this study for three dimensional structures. After this research was completed, we became aware that the pioneering work on these gels [7] included an observation of three dimensional swelling of a spherical gel. A quantitative analysis of the three dimensional results, however, was not presented.

The functional form of Equation 3 cannot correctly represent the final stages of the swelling process. As the gel approaches its maximum swelling potential, it always returns to its original shape. The fold pattern dissolves entirely. $k(t)$ must approach 0 as time approaches infinity. Typically, a gel cylinder with a starting diameter of 38 mm will take approximately 5 days to reach its maximum swollen size. The power law cannot be expected to be applicable once the structural changes are occurring on a scale comparable to the size of the gel itself.

In previous experimental work with two dimensional cases, the inverse square root power law was found to break down for longer times, though for a different reason. Since those gels were rigidly tethered on one side, there was a permanent pattern deformation on the other free surface of the gel. Thus, $k(t)$ always approaches a finite number after long periods of time. For example, a 15 cm x 15 cm gel plate showed a constant $\lambda \approx 1.5$ cm from t = 10 hrs to more than 100 days. This strongly suggests that the equilibrium value of $k(t)$ is not zero for these tethered two dimensional gels. In our study, however, all surfaces were free and $k(t)$ eventually approached zero.

It is interesting to question whether this inverse square root dependence is valid near the beginning of the swelling. There is no reason to assume that diffusion is the dominant physical process at the earliest times.

No data were available for $k(t)$ for times less than 45 minutes. Our study of the initial swelling of the gels is shown in Figure 9. The fitted curve for this early stage of swelling gave an exponent of n = -1.07. The evolution of $k(t)$ at times less than 12 minutes was found to be more rapid than expected purely from diffusion. The surface roughening at earlier times appears to follow the more

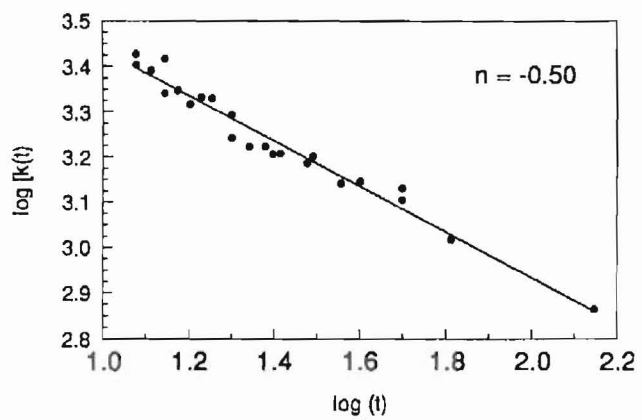

Figure 8
Evolution of fold pattern of all three gel sizes. The solid line is a straight line fit with slope = -0.50

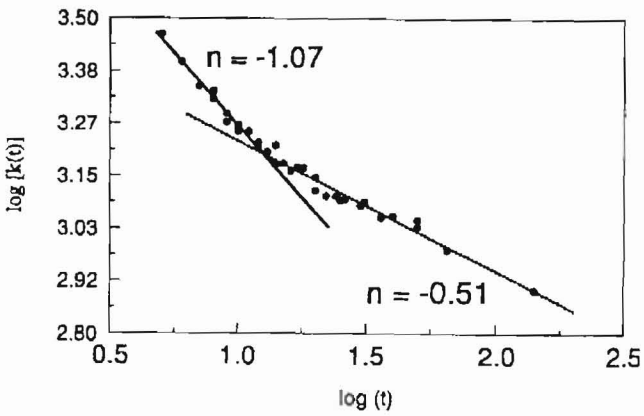

Figure 9
Evolution of fold pattern: cross over from $k(t) \alpha 1/t$ at early times to $k(t) \alpha 1/\sqrt{t}$ behavior at intermediate times.

rapid evolution

$$k(t) \alpha 1/t \quad . \qquad (4)$$

This faster kinetic behavior is a new result.

After several minutes, the swelling follows the expected diffusional rate of Equation 3. Although the transition between these two kinds of kinetic behavior is not physically sharp, the cross over can be seen in the graph of the $\log[k(t)]$ vs $\log(t)$.

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Dr. Narendra K. Jaggi
Laboratory for Materials Physics
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Bloomington, IL 61702-2902

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Physics Department
Guilford College
Greensboro, NC 27410
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Three-Dimensional Structural Evolution in Swelling Gels: The Fold Pattern Formation on the Edges of Unrestrained Gel Cylinders

INTRODUCTION

Polyelectrolyte gels are a class of polymers consisting of a crosslinked network with ionizable groups and a liquid solvent. These gels have recently attracted considerable attention because they exhibit giant electromotility, viz. macroscopic swelling and subsequent bending in response to modest electric fields [1-7]. Much research has been conducted to explore the potential of these gels as artificial muscle systems [5-7]. The as-synthesized copolymer gel is first equilibrated in an aqueous environment, without any ambient electric fields, before it is ready to be used in electromotility applications. Typically, experimenters have used thin rod-shaped gel specimens because they are interested in simulating the action of muscle fibers [3-7]. During this zero-field equilibration in water, these gel rods swell substantially (up to 60x their initial volume), but appear homogeneous and retain the geometry of the initial gel specimen. While experimenting with much larger cylindrical samples, however, we have discovered that the swelling at intermediate stages is in fact quite inhomogeneous. These gels undergo novel structural swelling patterns that are complex and elegant. In this paper, we describe these novel structures, their kinetics, and our qualitative understanding of this phenomenon.

Pattern formation on the surfaces of swelling gels, however, is not an entirely new phenomenon. The inhomogeneous swelling and the consequent roughening on the surface of polyacrylamide gel was first observed by Tanaka et al. [15,20,21]. This phenomenon has since been studied in substantial detail by many researchers, and a semiquantitative understanding of these patterns has emerged [8-21]. These patterns are not entirely random and are self-similarly reproducing as the gel continues to swell.

One theoretical model is based on a network of mechanical springs working against friction to simulate the swelling process in 1+1 dimensions [8]. Several theories are based on the minimization of free energy from the osmotic pressure of the diffusional process [10,14]. Models based on theories of general elasticity and the mechanical instabilities of the gel have also been proposed

[12,19]. All of these theoretical models provide generally acceptable agreement with experimental observations. Due to the complexity of these models (elastic constraints and diffusional osmotic pressures in three-dimensional space), theory has been limited to two-dimensional surfaces. Even in this restricted 2-D case, approximations had to be made in order to make significant progress.

In order to make quantitative contact with these model predictions, most experimental work has therefore naturally focused on the two-dimensional structural patterns [9,16-18]. These experiments have been conducted using thin gel slabs which are constrained on one surface by covalently tethering to a substrate. This set-up allows one to directly observe the patterns on the free, unrestrained surface of the swelling gel, characterize them in full detail, and compare with theoretical predictions.

Due to recent massive advances in the computational speeds of relatively inexpensive computing platforms, it may now be possible to analyze these complex swelling structures in three-dimensional form. Little information is available, however, about inhomogeneous three-dimensional swelling of gel samples with different initial geometries. Apart from some early observations on small spherical gels [15], three-dimensional swelling patterns have been largely ignored and are the subject of this paper. Specifically, we are interested in knowing whether there is a fundamental difference, either in the structure or the kinetic behavior, when there is a crossover from two to three spatial dimensions. Thus, we began experimental work with right cylindrical gel pieces of varying size. This specific geometry provides an opportunity to study the pattern formation at the edges of the unrestrained gel cylinder. We have discovered novel, pretty, and complex patterns in this geometry and what appears to be a fundamentally different kinetic behavior. These results are described in the rest of this brief report.

MATERIALS & METHODS

Experiments were conducted using crosslinked Poly(AA-NaA/AAm) copolymer gels. The procedure for the synthesis of the gels was similar to earlier work [9,18,20,21]. The crosslinking agent was N,N'-methylenebisacrylamide (BIS) and the free radical polymerization was initialized using N,N,N',N'-tetramethylenediamine. The ratio AA:NaA:BIS remained constant at 4:1:1? to produce stable swelling structures. Instead of preparing thin slabs, the gels were initially formed into right cylindrical pieces of varying height (14-48 mm) and diameter (22-45 mm). The gels were then immersed in a large container of

deionized water and allowed to swell unrestrained. This moment of immersion is considered to be time t=0. Because the refractive index of the gel is nearly identical to that of water, it becomes essentially invisible when immersed. It was therefore necessary for qualitative observations and when making measurements to remove the gel from the water, record its image using a videocamera, and quickly return it to the water for continued swelling. Digital image enhancement was sometimes necessary for postprocessing of these images.

RESULTS & DISCUSSION

We first describe the morphology and the early time (t~minutes) evolution of the coarsening patterns on the free surfaces of the cylindrical gel. As expected, the observed patterns on the flat surfaces (top and bottom) are nearly identical to those reported by other workers on the free surface of a restrained gel slab [9,18,20]. At early times, the small curvature of the side walls of the cylinder has no significant effect, and the patterns on the side walls are identical to those on the flat surfaces. These self-similarly reproducing patterns resemble the familiar tree-like form, reported in previous literature [18] (Figure 1a.).

Eventually, however, there is a morphological change and the pattern evolves into the honeycomb-like pattern [16] (Figure 1b.). Although this pattern is not completely regular, each "unit cell" has an approximately hexagonal local shape. It has previously been claimed [18] that this honeycomb pattern of relatively ordered morphology develops only if the thin 2-D gel slab is rigidly bonded to a fixed substrate. This hexagonal pattern was previously thought to be stabilized only by the strong elastic constraint resulting from the rigid covalent tethering of the bottom surface of the gel slab. This conclusion was supported by the fact that the honeycomb-like pattern was not observed in small, swelling spherical gels [15,18]. In these unrestrained spherical gels, the swelling patterns were eventually eliminated, and the surface of the fully swollen gel was completely smooth. This present work on relatively large right cylindrical gels provides a counterexample to this claim. Our gel samples are not restrained, all surfaces are free to swell, and the patterns are again transient. Yet, the more ordered, honeycomb pattern is indeed observed on the surfaces of the cylinder at later times. The rigid bonding of one side of a gel does not appear to be a prerequisite for the formation of the honeycomb pattern [18]. It is possible that, for thicker samples, the unswollen gel layer beneath the surface provides a constraint that is sufficient to produce these honeycomb-like patterns.

Upon close microscopic examination, the unit cells of the pattern appear to be convex folds that meet each neighboring cell in a cusp. These configurations have therefore also been described as surface fold patterns [9,18,19]. Although the fold pattern is not strictly periodic, one can easily identify a dominant length scale (λ) over which this pattern repeats. At any given time (t), we characterize the fold pattern by a wavenumber k(t), where $k=2\pi/\lambda(t)$. The video images were graphically analyzed to find the dominant length scale $\lambda(t)$, or equivalently, the characteristic wavenumber k(t). The evolution kinetics is then conveniently described by the time dependence of k(t). A typical result of k(t) vs. t is shown in figure 2. The data was fit to a power law, viz. $k(t)=ct^n$, providing a best-fit exponent of n = -0.52. This relationship ($k \propto t^{-1/2}$) is predicted by various theoretical models [10,19] and has also been observed experimentally in 2-D tethered gels [9,18]. In this case, though, k(t) will eventually approach zero, instead of asymptotically approaching a nonzero constant value as seen in the case for a restrained gel slab [18]. Because none of the surfaces of the gel cylinder have been restrained, the fold pattern is transient and when fully swollen, the gel returns to its initial shape and smooth surface. Apart from these two matters of detail, discussed above, the structure and evolution of the fold pattern on the surfaces of the cylinder appear to be in general agreement with past theoretical and experimental work.

We now present the results that appear to be novel and specific to the three-dimensional geometry of the gel samples. All results in the following correspond to typical samples of the same initial size, viz. right cylindrical gels with 38 mm diameter. In addition to the coarsening on the surface of the gel, there are unusual structural developments on the top and bottom edges of the cylinder. At intermediate stages of growth, these specimens display interesting, complex, and elegant structures that are rich in detail with a delicate aesthetic quality. Figure 3. shows one view of the gel at a certain stage of swelling, resembling an ornate, transparent crystal or glass sculpture. As the gel cylinder continues to swell, it produces an ever-evolving artistic forum.

It is quite difficult to mathematically parameterize these complex three-dimensional shapes. Clearly, the most appropriate method to convey the structure and its evolution is to play back the time sequence of video images taken from different angles during the swelling process. Since this is clearly not possible, we show in Figure 4. a few representative pictures of the structural evolution. The three-petal, orchid-like structure seen in Figure 3. develops in about 20 hours of swelling. Continued swelling for approximately another two days returns the gel to its original cylindrical shape with perfectly smooth

surfaces. Apart from the fact that the gel is approximately 50 times its original volume, the shape is essentially identical to what it was at time t=o.

Despite the apparent complexity of the pattern, careful observation of different samples clearly shows that the sequence of structural evolution is extremely reproducible. In particular, the shape transformations are basically identical for similar initial gel geometries. Two separate gels with similar initial geometries will evolve through the same structural transitions. Also, each gel identically follows the same "path" of structural changes each time it is swollen. At any stage during swelling, the gel can be removed from the water and allowed to return to its original unswollen state. If the gel is then replaced in water, it evolves following the same "path" of structural changes and patterns as before. This suggests a more or less deterministic theoretical model for these patterns.

There is one aspect of the structure, however, which lends itself to a simple mathematical representation, viz. the pattern on the edge of the cylinder. Figure 5. shows the top view of the gel cylinder as this pattern evolves from a) 10 minutes to b) 2 hours. This edge pattern is quite regular and nearly periodic, so that one can simply count the total number of folds or fringes, N. It is possible to characterize the growth of the gel by the number of these fringes, N(t), around the edge of the cylinder at any time. At early stages of swelling, the fringe pattern is distinguished by a small λ, or large N. At later stages, the pattern is composed of an increased λ and smaller N. The number of these fringes N(t) is seen to decrease monotonically with time.

Clearly, though, N(t) cannot be arbitrarily and infinitely large at the earliest times of swelling. There must be a cut-off length scale for which this description breaks down, as there are a finite number of fringes at the immediate origin of swelling. Also, nearly all previous experimental work with two-dimensional surfaces studied the macroscopic swelling patterns for later stages of growth (t>45 min.) [9,18,20]. Little is known about the swelling structures for very early times. It was thus necessary to microscopically observe the swelling patterns at these early times. Almost immediately upon contact with the solvent, fine gear-tooth-like structures form in a regular, nearly periodic pattern on the top and bottom edges. As the gel continues to swell, however, those gear-tooth-like features quickly evolve into a more rounded and full, three-dimensional "fringe" pattern. (Figure 5a.) This pattern self-similarly reproduces as these fringes or folds grow into themselves, gaining mass and volume due to the swelling uptake of the solvent. (Figure 5b.) Eventually, this rapid growth begins to take-over the structural formation of the entire gel cylinder as the

actual shape is dominated by the swelling of this fringe pattern at the edges.

The evolution of this fringe pattern at the edges was also quantitatively analyzed to understand the physical process. The total number of folds or fringes (N) around the top edge of the gel cylinder was measured during the swelling process. Figure 6. shows the resulting graph of N(t) vs. t as the number of fringes decreases monotonically with time. As might be expected, the fringes evolve following the form $N(t) \propto 1/\sqrt{t}$. However, it is interesting to question whether this $N(t) \propto 1/\sqrt{t}$ dependence is valid for earlier swelling times as well. As mentioned before, past experimental work has focused on the macroscopic swelling patterns for later stages of growth. It is important to understand the initial aspects of the swelling process as well. Figure 7. shows the results of plotting log[N(t)] vs. log(t) for early swelling times ($t<12$ min.) and the resulting exponent of -1. It appears that the fringe pattern evolves more rapidly than expected, following the relationship $N(t) \propto 1/t$. After several minutes, however, the fringe pattern follows the expected diffusional rate of $N(t) \propto 1/\sqrt{t}$. An interesting aspect in the structural evolution is this crossover from an exponent of $n=-1$ to $n=-1/2$. Figure 8. shows a graph of log[N(t)] vs. log(t), illustrating the crossover between the two stages. This change in kinetic behavior is a new result that has not previously been reported.

Although this crossover in swelling dynamics is clearly distinguished in the graph, it is not a sudden change that is visibly apparent. However, this is due to the evolving nature of the folds themselves. It must be noted that it is not the actual wavenumber that is being plotted, but rather the total number of folds N(t). If necessary, the value of N(t) can be converted to a characteristic edge wavenumber $k_{edge}(t)$. If this edge wavenumber k(t) is calculated and plotted, the crossover is seen to disappear and the relationship $k(t) \propto t^{-1}$ is valid for all times. (Figure 9.) This result is one of the fundamental kinetic differences between two and three-dimensional swelling patterns. The reason for this crossover can be explained by the characterization of the wavenumber itself. The wavenumber is defined by $k(t)=2\pi/\lambda$ where $\lambda=L/N$ (L being the total length over which the pattern repeats). At short times for which the fringes are relatively small, L is approximately equal to the circumference ($2\pi r$) of the cylinder and $k(t) \approx N/r$. But as the folds continue to swell, L becomes much greater than the circumference, and k(t) is no longer proportional to N, since $k(t)=2\pi N/L$. It is at this point that the crossover occurs, as the amplitude of the folds significantly increases. (The problem still remains, though, of accurately measuring L and hence k(t). Because the fringes are three-dimensional and continually growing, it is difficult to find the total length (L) of the fringe pattern at any given time.)

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Dependence of Surface Patterns on the Elastic Moduli of Polyelectrolyte Gels

I. INTRODUCTION

The topic of pattern formation in various media has been of general interest in recent years. Specifically, there has been considerable interest in the inhomogeneous swelling of copolymer polyelectrolyte gels and their subsequent surface pattern formations. The morphology of the fold patterns observed on the surface of tethered gel slabs has been studied extensively. Theoretical models based on the elastic constraints of the gel have been proposed and provide generally acceptable confirmations with experimental observations. However, it appears that these swelling patterns and their evolution are not completely understood. Although the theoretical model for the underlying physical process of pattern development based on elasticity does exist, it does not provide an extensive explanation for possible pattern variations. While these gels do swell inhomgeneously, there are other gel compositons that do not form pattern and swell homogeneously. General theories for why gels may or may not swell homogeneously are not completely understood. It is therefore important to study cases for which there is a wide variance in the pattern formation of these gels.

During previous experiments with pattern formations on gel cylinders, we noticed slight variations in the surface patterns at early times. It appeared that these small differences in pattern formation were caused by inconsistencies in the initial chemical composition of the gel. We therefore became interested in the possibility of significantly noticeable pattern variations in these swelling gels. Specifically, we wanted to see if variant patterns could be produced by different chemical compositions of the gel. A variation of the initial chemical make-up of the gel could possibly determine the kind of pattern produced during swelling.

Because of the chemical complexity of these gels, we focused on changing only one aspect of the gel's composition, namely the concentration of the cross-linking agent, N,N-methylenebisacrylamide (BIS). Increasing the concentration of the BIS crosslinker effectively increases the frequency with which the

polymer chains are connected to each other. As more polymer chains become crosslinked together, the entire network becomes more rigid and the elasticity of the gel is reduced. Thus, increasing the BIS concentration effectively changes the elasticity of the gel. We therefore focus on the variance of pattern formations caused by the differing elastic constraints in the initial chemical composition of the gel.

The transformations and surface patterns produced by a swelling polymer gel are unstable and will eventually disappear once equilibrium with the outside solvent is reached. Restraining the gel (tethering one side to a fixed plane) during swelling, though, will result in a stable pattern on the surface. Most previous experimental work has utilized this method of constraint to study pattern formation in gels. Thus, experimentation has been forced to focus mainly on larger gel slabs requiring a long period of time ($t > 100$ hrs.) to form substantial, visible patterns on the surface. Little attention has been paid to the initial surface structures at short times ($t < 300$ s). We therefore intend to study the microscopic surface pattern formation from initial swelling.

II. MATERIALS & METHODS

Experiments were conducted with crosslinked polyacrylamide/sodium acrylate [Poly(AA-NaA/AAm)] copolymer gels. Details of the synthesis and composition of these gels was similar to previous work.[] The crosslinking agent of the polymer chains was N,N'-methylenebisacrylamide (BIS), and the free radical polymerization was initialized using N,N,N',N'-tetramethylenediamine (Temed). Gel samples were prepared with various concentrations of the BIS crosslinker, ranging from 0.0005 to 0.006 mols. All other initial chemical aspects were kept constant for the gel samples.

Because we intended to study the evolution of these pattern formations, it was necessary to make continual observations. This was easily accomplished by viewing the early time swelling through video-microscopy. This allowed for the entire swelling process to be viewed and recorded. These qualitative observations of the pattern formation were made from the top of each sample which was an unrestrained, flat surface, unaffected by the boundary conditions of the gel's edges. Subsequent digital enhancement was utilized to further analyze the pattern formations.

III. RESULTS & DISCUSSION

It is presumed that varying the concentration of the BIS crosslinker should have a direct influence on the gel's elasticity. This initial condition of elasticity is one of the parameters responsible for the structural patterns that form during swelling. Changing the BIS concentration in the gel should therefore decidedly alter the initial surface pattern formation on the surface. Indeed, there is a definite variation in the pattern formation due to this initial variance of the elastic constant of the gel. Figure 1.shows the gradual change in these patterns. In this series, the BIS concentration has been increased from 0.0005 to 0.006 mols. Each gel sample in this series has been allowed to swell for approximately 3 minutes. The gel sample with a typically lower BIS concentration of 0.0005 mols produces the expected quasi-hexagonal pattern that has been observed by other workers []. At this short time, the pattern has not developed into the full honeycomb-like form. Yet there is a definite sense of the formation of the unit cells and the characteristic angle of 120^0 connecting the cusps. However, as the BIS concentration is increased, the patterns begin to lose this connectivity of the fold lines between unit cells. Eventually, at the higher BIS concentration of 0.006 mols, the honeycomb-like pattern is not even distinguishable. At this level of decreased elasticity, all that remains of the pattern are the unconnected fold lines that used to form the unit cellsThus, the typical pattern formation appears to "dissolve" or "fade away" as the BIS concentration, and the elastic constraint of the gel, are effectively increased. This is one central result of this work.

If the BIS concentration is increased higher (0.008 - 0.009 mols), the pattern decays entirely. At this level of extreme elastic constraint, there is an absence of any pattern formation and the gel swells nearly homogeneously. With this chemical composition, the polymer chains are quite rigid and inelastic. Thus, there is little capacity for swelling at all. Because the elastic constraint of the gel is strong enough to eliminate the formation of patterns on the surface, it does not provide much potential for swelling. In fact, the gel itself becomes "brittle" and breaks apart during swelling due to this extreme inelasticity.

Although the pattern formations on gel samples with higher BIS concentrations are noticeably different after only a few minutes of swelling, at very early times ($t < 60$ s) they appear quite similar. During this immediate swelling period, the surface patterns on all the gel samples appear to evolve in a similar manner. Within the first few seconds of swelling, the tiny, tree-like pattern appears on the surface and begins to grow rapidly. These "branches" of unconnected unit cells grow into each other, causing the surface structural formation to increase in size but maintain its original pattern. This immediate development of the surface

pattern, though, is common to both the higher and lower BIS concentrations. (Figure 2.) At lower BIS concentrations, the surface pattern continues to grow into itself in the same manner as the fold lines continue to connect and form the more ordered, honeycomb-like unit cells. At higher BIS concentrations, however, the original tree-like pattern begins to dissolve into the series of disconnected lines as the gel continues to swell. Although both samples begin to swell in the same manner, they quickly evolve into different pattern variations.

The observed pattern formations at early times might be expected from general theoretical models of swelling. Increasing the BIS crosslinking agent provides a greater elastic constraint on the gel as it swells. As each unit cell from the original quasi-hexagonal pattern attempts to swell, it is restrained by the gel's increased elasticity. Thus, the pattern begins to dissolve with increased elastic constraints to show only the unconnected lines that once formed the hexagonal cells. Increasing the BIS concentration past a critical value (0.008 mols) appears to eliminate the pattern almost entirely. During the first few seconds of water diffusion into the gel, however, the swelling of the surface is presumably not fully constrained by the gel's elasticity. Thus, it might be possible for samples of varying elastic constraint to behave similarly. Once the gel begins to swell for about one minute, though, it becomes more fully constrained by the greater inelasticity as the water pushes against the polymer chains. It is at this point that the pattern formation begins to dissolve for gel samples with higher BIS concentrations and the increased elastic constraint does not permit the typical fold pattern formation on the surface.

Evidence for the increased elastic constraint of gels with higher BIS concentrations is also observed in the time required for the surface pattern to disappear in the absence of a solvent. A gel sample of low BIS concentration that has been swollen for five minutes will take several minutes for the surface pattern to disappear. The surface pattern of a gel with high BIS concentration, however, will disappear in a few seconds. The stronger elastic constraint of the gel quickly restores it to its original homogeneity when removed from the water.

In the course of these studies, we also observed an interesting swelling phenomenon. During the early stages of swelling, some gels exhibited an entirely new mode of pattern formation. Instead of the steady and constant evolution of all previous surface patterns observed, these patterns appeared to instantly "pop" into the surface of the gel. These gels would swell normally for several seconds forming the normal tree-like pattens of early morphology.

Then, fold lines would suddenly appear on a scale much larger than the developing pattern. It appeared as if the pattern formation had skipped an amount of time and gone immediately to a slightly later time in the evolution of the pattern formation. After these fold lines "pop" into the gel, this larger scaled pattern then continues to grow as before.

Furthermore, this unusual mode of pattern formation also exhibits what could be called a "memory effect." This stage at which the pattern immediately "pops" into the surface of the gel is identically reproducible. The gel can be taken out of water and allowed to swell again. Remarkably, the pattern of fold lines will "pop" into place in exactly the same manner. The pattern of these fold lines on the surface will be identical to the pattern formed from a previous trial. The gel can, in effect, identically "remember" this pattern and its position - as if it were "frozen" into the surface of the gel. It is possible that this frozen position is actually the cause of this mode of pattern evolution. It must be noted that this form of pattern evolution was never seen in newly prepared gels. This formation was only observed for gels that had previously been swollen to some extent and allowed to return to their initial condition. It might be possible in this state of shrinking for the gel to actually "freeze in" a pattern on the surface. Then, at some early stage of swelling, the pattern evolution might skip normal steps and "jump" to that later stage of the pattern frozen into the surface. This could possible account for the identical reproducibility of this pattern evolution for consecutive swelling trials.

IV. CONCLUSION

We have examined the effect of varying the cross-linking concentration in copolymer gels upon the initial formation of surface patterns. It appears that increasing the BIS cross-linking concentration has a direct effect on the surface pattern formations. As the BIS concentration and the elastic constraint of the gel is increased, the patterns become less distinct and begin to dissolve into a configuration of broken fold lines. Gel samples with effectively high concentrations of BIS show no pattern development at all. And although there are definite pattern differences for samples with varying BIS concentrations, they appear to swell similarly at very early times. Furthermore, we have observed an unusual mode of pattern formation in which the gel apparently has stored a memory of previous patterns. Although no theory of elasticity exactly predicts these pattern variations, we are currently attempting to model this swelling behavior.

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